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STUDY OF WATER VAPOR ABSORPTION LINES IN  
THE NEAR INFRARED

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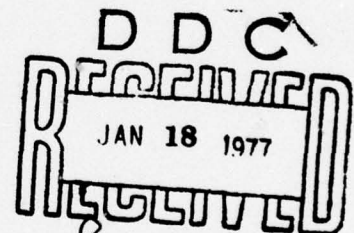
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Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

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Covering the Period  
May 1, 1973 to June 30, 1975

STUDY OF WATER VAPOR ABSORPTION LINES  
IN THE NEAR INFRARED

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# ABSTRACT

5000  
The purpose of this work was to develop a highly stable spin flip Raman laser that could be tuned through the 5 $\mu$  region in order to study water vapor absorption lines. The pressure broadening coefficients for various buffer gases when added to water was measured with this system. A general technique was devised to measure the shape of absorption lines well out onto the wings to determine if there were any deviation from a Lorentzian lineshape. In addition, theoretical work was done on the interaction of a radiation field with molecules undergoing a collision. A formulation was developed and used to treat the case of a collision between two noble gases.

This work has been done collaboratively by:

M.A. Guerra, M. Ketabi, A. Sanchez, R. Sharma, R.R. Hart, M. Feld, and A. Javan.

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key words: water vapor lines; absorption lineshapes; spin flip Raman laser; tunable 5 $\mu$  radiation; non-Lorentzian lineshapes; pressure broadening coefficients.

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## INTRODUCTION

This is the final report of a research program which began in June of 1973 at the MIT Optical and Infrared Laser Laboratories. In this program, the experimental studies were planned to evolve in several phases. In its first phase, the major effort was directed toward meeting two intimately related objectives. The first consisted of construction of the necessary frequency tunable light sources, initially in the  $5\mu$  region and later in the  $3\mu$  region. The second objective, which progressed in parallel with the first, consisted of establishing the necessary spectroscopic method for accurate measurements of line-shape features on the "wings" of the water vapor absorption lines. For this it is to be recognized that the conventional spectroscopic methods are unsuitable and special approaches needed to be developed and perfected.

The first phase of the planned program was successfully completed. A unique frequency tunable spin flip laser engineered for single mode operation and free from frequency mode jumping and amplitude instability was designed and constructed. This laser utilizes a permanent magnet with a field gradient for frequency tuning and two specially designed highly stable c.w. CO lasers. The CO lasers and the rest of the spin flip assembly are mounted on a highly stable and vibration free platform to provide isolation from microphonic



disturbances which are usually major sources of frequency jitters. Course frequency tuning is achieved via an accurate and well-balanced mechanical device (See Section 2). Moreover, this laser system has already been used and tested in an initial experiment dealing with measurements of water vapor line-broadening by buffer gases along with an actual observation in the atmosphere. (This work was published in the Journal of Chemical Physics. See Appendix I.) Appendix II contains a detailed analysis of the results presented in that work.

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To accomplish our second objective, a special "Two Arm" balanced bridge was designed in which the radiation from the output of a fixed frequency CO laser is transmitted through one arm of the bridge, and the frequency tunable spin flip radiation is transmitted through the second arm. The bridge is capable of making corrections for amplitude variation of the spin flip laser as its frequency is tuned over a wide portion of the spectrum. It can determine accurate lineshape features along with the actual magnitudes of the absorption coefficient on the wings of the absorption lines, both in air as well as in a gaseous mixture consisting of known amounts of water vapor and buffer gases.

In addition, we had also performed the preliminary work towards doubling the frequency of the tunable laser from

the  $5\mu$  into the  $2.5\mu$  region of the spectrum. This is done with a Proustite crystal and harmonic generation.

Section 1 of this report gives a brief account of the "balanced-bridge" that was to be used in the continuation of the work, along with an example for estimating the bridge parameters. Section 2 gives a brief account of the spin flip laser developed for this experiment. Appendix I describes measurements of line broadening coefficients for several water vapor lines. This was done with the spin flip laser developed for this program.

It should also be noted that in addition to the past experimental efforts, the activities under this program supported a sizable theoretical work by Professor R. Sharma. The theory has dealt with an attempt to eventually determine lineshape features on the wings of the water vapor lines with the aid of elaborate collision and molecular scattering theory. The theory is extremely complex and has required a gradual development of calculational procedures. These relate to formulation of the interaction of a water molecule with an applied radiation at a tunable frequency while the water molecule suffers a collision. In other words, the interaction is formulated for the duration of time when a collision is in progress, rather than during the mean free time in between two collisions. In an initial attempt, Professor Sharma has developed the theory for simple examples involving collisions between two noble gases. The results of this work is shown in Appendix III.

## Section 1. - Studies of Wings of Water Vapor Lines

Having completed a set of measurements of lineshape features in the vicinity of water vapor resonances with the tunable spin flip Raman (SFR) laser developed for this program, a novel two arm balanced bridge was designed in which the transmission at a fixed frequency on the wing of the line could be measured simultaneously with the transmission at a tunable frequency in the vicinity of an absorption line.

The tunable  $5\mu$  c.w. spin flip Raman laser could be transmitted through one arm of the bridge and used to probe the absorption line at various points, from line center up to a detuning of  $1.2\text{ cm}^{-1}$ . A fixed frequency stable CO laser would then be transmitted through a longer arm and used both as a reference and for monitoring the absorption on the wing. (In the example given below, the CO frequency is  $2.7\text{ cm}^{-1}$  away from the peak). The tunable frequency laser radiation is continually balanced against the fixed frequency reference CO laser at the input of the bridge. The unbalanced signals at the output are recorded in the presence of air, or water vapor along with buffer gases introduced in the bridge. This bridge overcomes a major difficulty in lineshape measurements arising from variation of the tunable frequency laser power as its frequency is tuned over a wide range.

Our experiments, obtained values for nitrogen and self-broadening coefficients of water vapor resonances on several low J transitions which agreed closely with the theoretical predictions. For the initial measurement, we have



chosen a line, (000),  $5_{32} \rightarrow (010)$ ,  $6_{43}$ , which falls at 1889.58  $\text{cm}^{-1}$ , for the fact that it is well isolated from other transitions. It follows from our earlier work that the theoretical values of 6.3 (nitrogen-broadening) and 31 (self-broadening) MHz/torr are reliable near line center. Measurements by Long et al<sup>(4)</sup> indicate that the absorption in the wings is considerably larger than that predicted from a Lorentzian line-shape. Therefore, we can assume a Lorentzian behavior for the absorption line to obtain a lower limit for the absorption coefficient there.

The absorption coefficient can be written as:

$$\gamma = \frac{8\pi^2 |\mu_{ij}|^2 \nu}{3hc} Nf \left(1 - e^{-\frac{h\nu_0}{kT}}\right) \left[ \frac{\frac{1}{2\pi\tau}}{(\nu - \nu_0)^2 + \left(\frac{1}{2\pi\tau}\right)^2} \right] \quad (1)$$

where  $\mu_{ij}$  is the matrix element of dipole transition,  $\nu$  and  $\nu_0$  are the laser frequency and the center frequency of the transition, respectively,  $Nf$  is the density of molecules in the desired rotational-vibrational level, and  $\frac{1}{2\pi\tau}$  is the half width at half height of the absorption line. If the line is broadened with nitrogen to the extent that the contribution of nitrogen broadening to the overall linewidth is much larger than that due to self broadening, then the absorption coefficient for the 1889.58  $\text{cm}^{-1}$  line is given (in  $\text{cm}^{-1}$ ) by

$$\gamma = \alpha \frac{3.2 \times 10^6 P_N P_{H_2O}}{(\nu - \nu_0)^2 + (3.2 \times 10^6 P_N)^2} \quad (2)$$

where  $P_N$  and  $P_{H_2O}$ , the nitrogen and water vapor partial pressures are measured in Torr, and  $\alpha = 2 \times 10^7$ . The addition of nitrogen broadens the line in such a way that the absorption at the peak decreases while absorption at the wings increases. Therefore, the absorption coefficients at the peak and at the wings  $2.7 \text{ cm}^{-1}$  away from the peak will be

$$\gamma_{\text{peak}} = \frac{P_{H_2O}}{3.2 \times 10^6 P_N} \quad (3)$$

$$\gamma_{\text{wing}} = \alpha \frac{3.2 \times 10^6 P_N P_{H_2O}}{(\nu - \nu_0)^2} \quad (4)$$

Since the absorption coefficient at the peak is much greater than that at the wing, we planned to use an experimental arrangement consisting of two cells, a short cell to probe the peak absorption and a long cell to probe the wing absorption, connected to a common reservoir (See Figure 1). If we restrict ourselves to total pressures below 5 atmospheres, then a 2 meter long cell in conjunction with a cell of length 10 cm could have the same absorption. In this case the absorption in each cell will be about 15% at 5 atmospheres of  $N_2$  and 7 torr of  $H_2O$ .

The experimental arrangement is shown in Figure 1. The CO and SFR lasers are balanced before they enter the "two arm" bridge and the relative intensity is measured after they have passed through the cells. By detuning the SFR laser from the peak of the line, the absorption can be determined at several points along to the wing. The system is designed to cor-

rect for variation of SFR laser power as its frequency is tuned over a whole region. This is done by taking the ratio of intensities measured before and after the cells.



Section 2. - A Brief Account of the Spin Flip Laser  
Developed for the Water Vapor Studies.

Continuous spin-flip Raman lasers provide tunable radiation in the  $5\text{-}6\mu$  region of the spectrum. As is well known, they consist of a crystal of InSb cooled to liquid He temperatures, placed in an external magnetic field, and pumped with radiation from a CO laser. By varying the value of the magnetic field, we can vary the difference in frequency between the radiation which comes out of the crystal and that which was sent in from the CO laser. But in general this tunable radiation consists of a complex mode structure, which varies considerably as one tries to tune its frequency. Usually one cannot tune more than 200-300 MHz before the modes start jumping discontinuously in frequency. This mode jumping seriously limits the usefulness of the spin-flip Raman laser in high resolution spectroscopy.

In the first phase of our planned program we constructed and perfected a tunable spin-flip Raman laser with some unique properties. Rather than use the conventional superconducting magnet or electromagnet, we have made use of a permanent magnet in our system. This has resulted in a large savings in cost and considerable improvement in stability. The magnet is outfitted with tapered pole pieces, that is, their separation varies with height. By mounting the magnet on a moveable platform, we can move its position up or down

in relation to the crystal. In this way we vary the magnetic field and tune the frequency. This system is capable of quasi-continuous tuning over the range of 5-5.4 $\mu$ . Use of different crystals enable us to cover different ranges.

Our system is unique in that it can be tuned over 3 GHz all the while remaining a stable single mode. Thus, we are free from the mode jumping, which has plagued previous systems. This opens up all sorts of possibilities for high resolution spectroscopy of water vapor and other gases. We have also added a feedback loop to our system which reduces the frequency jitter. The whole spin flip assembly, which utilizes two highly stable CO lasers, is mounted on a special (and highly massive) shock-mount platform, providing an "ultimate" isolation against microphonic disturbances and hence much improvements of its frequency stability. The early work on this laser was done by one of our students (M. Guerra) along with S. Brueck and A. Mooradian at Lincoln Laboratory. Most of the improvements and higher frequency stability work were done at our MIT Optical and Infra-red Laser Laboratories.

Appendix I

WATER VAPOR LINE-SHAPE MEASUREMENTS AT  $5\mu$   
USING A TUNABLE SFR LASER<sup>+</sup>

M.A. Guerra, M. Ketabi, A. Sanchez<sup>\*</sup>, M.S. Feld<sup>\*\*</sup>, and A. Javan

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Knowledge of water vapor lineshapes is important for understanding atmospheric propagation. Past linewidth studies using microwave<sup>1</sup> and conventional infrared<sup>2,3</sup> techniques generally have agreed with detailed predictions<sup>4,5</sup> based on Anderson's theory<sup>6</sup> to within 20 or 30%, while some have differed by as much as 50%. Some recent broadening coefficients of infrared transitions obtained using tunable lasers have been found to be substantially less than predicted, theory and experiment<sup>7,8,9</sup> differing by factors between two and four. The present study, which uses a tunable c.w. spin-flip Raman (SFR) laser, obtains values of self and foreign gas broadening coefficients which agree well with theory. While discrepancies do exist between values predicted by Anderson's theory and those obtained experimentally, in general there does seem to be better agreement for those transitions of low J than for those of high J.

The experiment used a low-field permanent magnet SFR laser,<sup>10</sup> pumped by a 2 W stable single-mode CO laser. Pressure broadening coefficients were measured for the  $1884.57 \text{ cm}^{-1}$   $[000,5_{15} \rightarrow 010,6_{24}]$  and  $1889.58 \text{ cm}^{-1}$   $[000,5_{32} \rightarrow 010,6_{43}]$  transitions ( $\nu_2$  band). The CO laser oscillated on the  $P_{9-8}$  (12) line at  $1888.32 \text{ cm}^{-1}$ . The permanent magnet had tapered pole pieces and could be positioned so that the first Stokes line of the spin-flip radiation was near the water vapor absorption line. Fine tuning was done electronically using Helmholtz coils which produced a frequency tuning of 6.8 GHz. In SFR laser measurements of this type, a reliable frequency scale is essential. By means of the method of coincidences, a Fabry-Perot interferometer with adjustable mirror spacing was used to obtain a frequency calibration accurate to a few percent. 11.

The pump and SFR laser beams, which had orthogonal polarizations, were separated using a silicon beam splitter. A second piece of silicon divided the spin-flip radiation into two approximately equal parts. One was sent through an 80 cm absorption cell to a detector, the remainder was used as a reference. After processing by lock-in amplifiers, these signals were fed into a ratio divider. In this way amplitude variations caused by fluctuations in the spin-flip output were eliminated.

For the foreign gas broadening measurements the cell was kept in equilibrium with a distilled water reservoir maintained at 0°C, providing a constant 4.6 torr partial pressure of water vapor. After each addition of foreign gas it was found important to wait a sufficient amount of time, usually five minutes, to permit the gases to mix completely and come to equilibrium.

Typical lineshapes for foreign gas broadening are shown in Fig. 1. The results of the self and foreign gas broadening measurements are plotted in Fig. 2. The nitrogen and self-broadening coefficients predicted by Benedict and Kaplan<sup>4,5</sup> are in good agreement with our measured values (Table I).

This indicates that the anomalously high absorption in the wings of water vapor resonances reported recently<sup>11</sup> is due to non-Lorentzian behavior and not to unusually large broadening coefficients. Further experimental work on this point is underway.

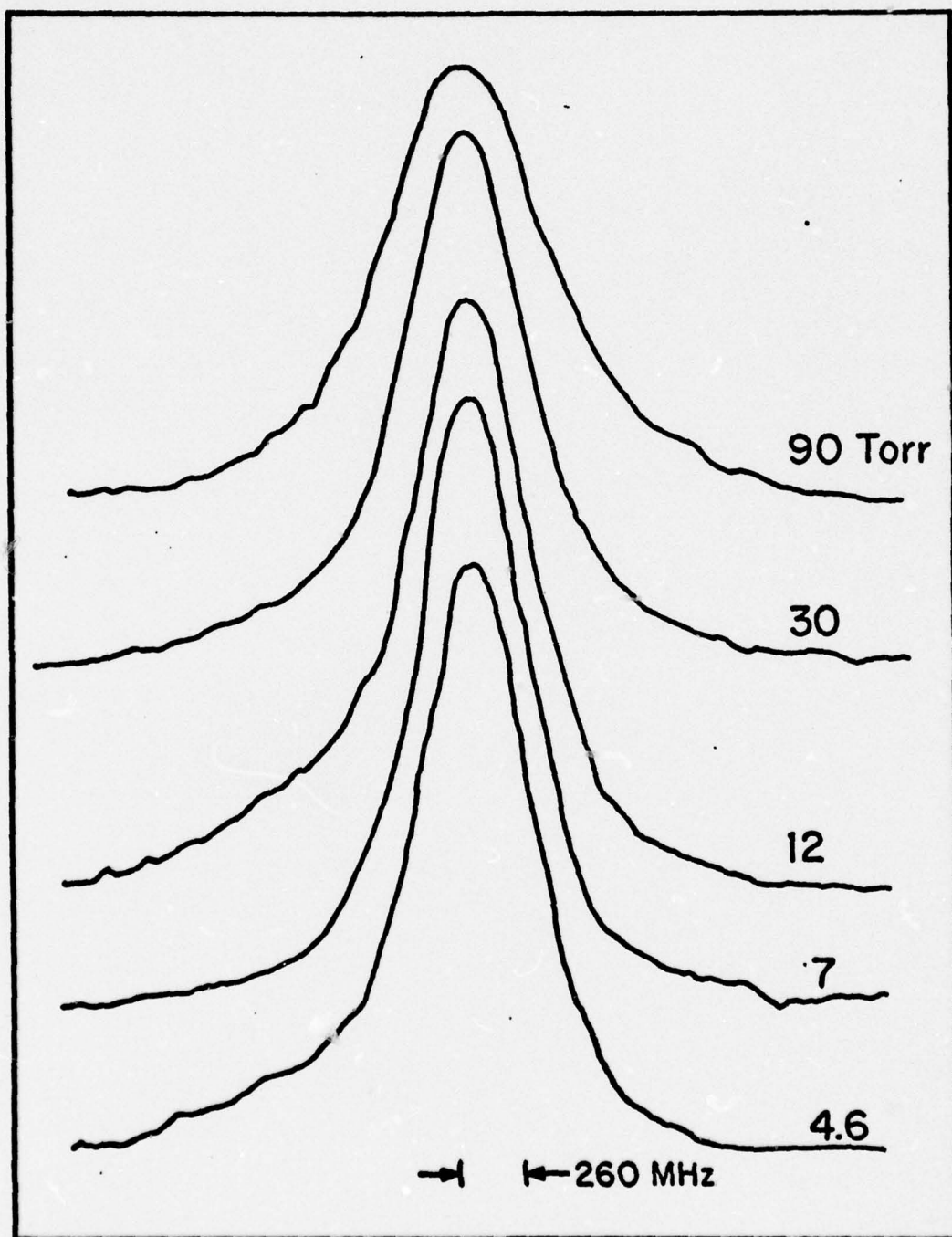
We have also studied the  $[1889.58 \text{ cm}^{-1}]$  transition of

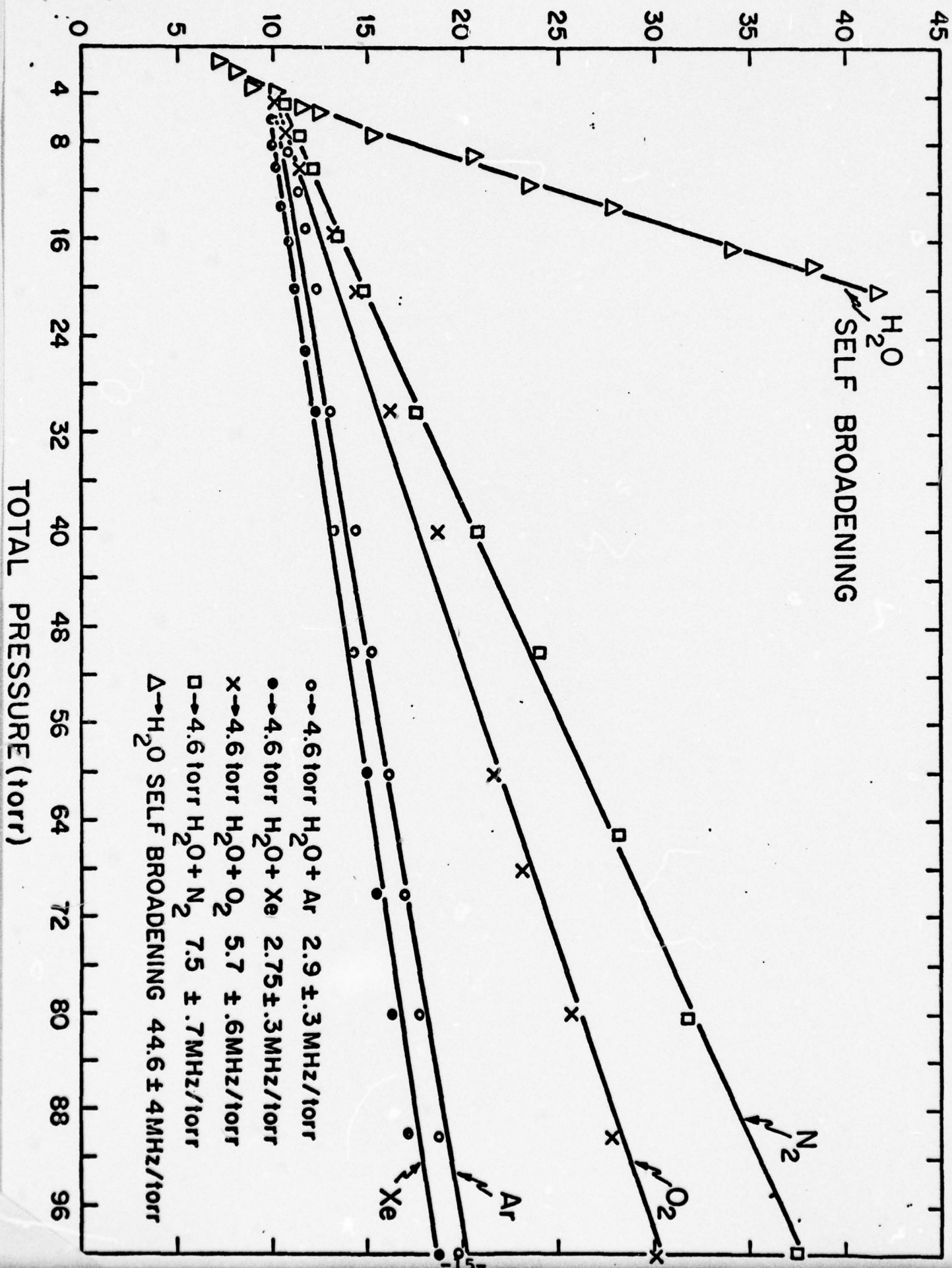
water vapor in the atmosphere at 22°C and 35% relative humidity (7 torr partial pressure). To avoid excessive absorption by this extremely strong line the air path of the spin-flip beam was reduced to 25 cm. Our measured air-broadening coefficient was  $8.1 \pm 1.3$  MHz/torr, as compared to the predicted value of 6.11 MHz/torr.<sup>12</sup> Since the ratio between self-broadening and nitrogen broadening in  $N_2O$  is known to be between 4 and 6.5<sup>4,5</sup> the self-broadening must be at least 24.4 MHz/torr and the actual value could greatly exceed that number. This differs markedly from the value of  $\sim 1.65$  MHz/torr, used by Patel.<sup>13</sup>

Measurements of the type presented here do not require a high degree of frequency stability. Nevertheless, the spin-flip laser is intrinsically capable of the stability necessary for high-resolution spectroscopy.<sup>14</sup> Detailed Fabry-Perot measurements have established that at times the SFR laser was multimoding. Steps have been taken to eliminate this problem and to incorporate a feedback stabilization network into the system.

We thank Richard Eng for helpful comments.







|                               | H <sub>2</sub> O | N <sub>2</sub> | O <sub>2</sub> | Ar      | Xe       |
|-------------------------------|------------------|----------------|----------------|---------|----------|
| Present Study                 | 44.6±4           | 7.5±0.7        | 5.7±0.6        | 2.9±0.3 | 2.75±0.2 |
| Theoretical Calculation (4,5) | 42.10            | 7.32           | —              | —       | —        |



### FIGURE CAPTIONS

Figure 1. Lineshapes for Argon broadening. Numbers indicated are total pressure (4.6 torr H<sub>2</sub>O constant partial pressure).

Figure 2. Pressure broadening lines of self and foreign gases.

Table I. Comparison between measured and predicted values of broadening coefficients for the 1884.57 cm<sup>-1</sup>, the units being MHz/torr.

Appendix II

COMPARISON WITH THEORY AND COLLECTION OF RESULTS  
OBTAINED BY OTHER INVESTIGATORS

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In this section our experimental measurements are compared with the results obtained by other investigators in different regions of the  $\text{H}_2\text{O}$  spectrum. These results are summarized in Table I. As can be seen, our results are in good agreement with the theoretical predictions of Benedict and Kaplan [4,5] which are based on Anderson's general theory of collision line broadening [6]. Based on this theory, we can understand some of the features of Table I. As one expects, the strong dipole-dipole forces responsible for  $\text{H}_2\text{O}$  self-broadening ( $\mu^0 = 1.87 \text{ D}$ ) lead to much greater widths than the ones that were found for  $\text{H}_2\text{O}-\text{N}_2$  broadening where the forces are dipole-quadrupole ( $Q_{\text{N}_2} = 2.62 \times 10^{-26} \text{ esu}$ ). The general course of the  $J_\tau$ -dependence is such that the linewidths in general decrease as  $J$  increases; at a given  $J$  the maximum width occurs for the levels of intermediate  $\tau$ ; and lines with high  $J$ , particularly those with  $|\tau| \approx J$ , have narrow linewidths which approach, as the lower limit, the kinetic-theory value.

The temperature dependence of the linewidth is given by the power law [4]

$$\gamma_T = \gamma_{300} \left(\frac{300}{T}\right)^n \quad (1)$$

where  $\gamma_T$  and  $\gamma_{300}$  are the full linewidths at temperatures  $T^\circ\text{K}$  and  $300^\circ\text{K}$  respectively and exponent  $n$  varies from line to line. The average value of  $n$  of all the lines weighed according to their intensity is  $n = 0.62$  for  $\text{H}_2\text{O}-\text{N}_2$  collisions and  $n = 0.896$



| Investigator(s)   | Ref. | Region<br>cm <sup>-1</sup> | Collision Broadening Coeff.<br>MHz/Torr |      |                                 |                  |                                   |      |         | Temp.<br>° C              | Method   | Transition |     |
|-------------------|------|----------------------------|---|------|---------------------------------|------------------|-----------------------------------|------|---------|---------------------------|--|------------|-----|
|                   |      |                            | H <sub>2</sub> O-H <sub>2</sub> O *     |      | H <sub>2</sub> O-N <sub>2</sub> |                  | H <sub>2</sub> O-air <sup>e</sup> |      |         |                           |  |            |     |
|                   |      |                            | Exp.                                    | Th.  | Exp.                            | Th. <sup>#</sup> | Exp.                              | Th.  | Exp.    |                           |  |            | Th. |
|                   |      |                            |   |      |                                 |                  |                                   |      |         |                           |  |            |     |
| Present Study     |      | 1884.57<br>1889.58         | 44.6                                    | 42.1 | 7.5                             | 7.32             | 6.92                              | 6.11 | Room    | SFR Laser                 | 5 <sub>1</sub> -4 <sub>1</sub> +6 <sub>2</sub> -2 <sub>2</sub> v <sub>2</sub><br>5 <sub>1</sub> +6 <sub>1</sub> v <sub>2</sub> |            |     |
| Izatt et al.      | 2    | 545.3                      | 35.4                                    | 27   | 7.1                             | 5.90             | 6.3                               | 6.0  | 80 Room | Conventional Spectroscopy | 7 <sub>1</sub> -6 <sub>1</sub> +8 <sub>2</sub> -0 <sub>2</sub> v <sub>2</sub>  |            |     |
| Ben-Aryeh         | 3    | 1961.19                    | 26                                      | 32   |                                 |                  |                                   |      | 127     |                           | 7 <sub>1</sub> -4 <sub>1</sub> +8 <sub>2</sub> -2 <sub>2</sub> v <sub>2</sub>  |            |     |
| Vasilevsky et al. | 15   | 4025.4                     | 40                                      |      |                                 |                  |                                   |      | Room    |                           | 5 <sub>1</sub> -5 <sub>1</sub> +6 <sub>2</sub> -2 <sub>2</sub> v <sub>3</sub>  |            |     |
| Adel              | 16   | 537.01<br>625.5            |   |      |                                 |                  | 9.45<br>8.67                      | ~5.7 | Room    |                           | 5 <sub>1</sub> +6 <sub>5</sub>   |            |     |
| Burch † et al.    | 17   | 1595                       |   |      |                                 |                  |                                   |      |         |                           |  |            |     |

\* Taken from Ref. 5

# Taken from Ref. 4

e Taken from Ref. 12

† Burch et al. have measured the ratio of self-broadening coefficient to nitrogen broadening coefficient to be 5±1.5.

| Investigator(s)  | Ref. | Region<br>cm <sup>-1</sup>    | Collision Broadening Coeff.<br>MHz/Torr |      |                                 |      |                      |                   | Temp.<br>° C | Method                           | Transition  |
|------------------|------|-------------------------------|---|------|---------------------------------|------|----------------------|-------------------|--------------|----------------------------------|---|
|                  |      |                               | H <sub>2</sub> O-H <sub>2</sub> O       |      | H <sub>2</sub> O-N <sub>2</sub> |      | H <sub>2</sub> O-air |                   |              |                                  |   |
|                  |      |                               | Exp.                                    | Th.  | Exp.                            | Th.  | Exp.                 | Th.               |              |                                  |   |
| Blum<br>et al.   | 7    | 1879.01<br>1879.34<br>1879.60 |   |      |                                 |      | 0.59<br>1.22<br>1.14 | 2.5<br>2.7<br>2.7 | Room         | Tun. Semi<br>Cond.diode<br>Laser | 15 <sub>-15</sub> →16 <sub>-15</sub> <sup>v2</sup><br>12 <sub>-9</sub> →13 <sub>-11</sub> <sup>v2</sup><br>12 <sub>-10</sub> →13 <sub>-10</sub> <sup>v2</sup> |
| Eng<br>et al.    | 18   | 1879.01                       |   |      | 0.57                            | ~2.5 |                      |                   | Room         | Tun. Semi<br>Cond.diode<br>Laser | 15 <sub>-15</sub> →16 <sub>-15</sub> <sup>v2</sup>  |
| Patel            | 19   | 1885.24                       |   |      |                                 |      | 3.44                 | 4.3               | Room         | SFR laser                        | 10 <sub>-6</sub> →11 <sub>-6</sub> v <sub>2</sub>   |
| Patel            | 13   | 1889.58                       | 1.7                                     | 35.2 |                                 |      |                      |                   | Room         | SFR laser                        | 5 <sub>1</sub> →6 <sub>1</sub> v <sub>2</sub>   |
| Kyhl<br>et al.   | 20   | 0.744                         |   |      |                                 |      | 8.7                  | ~7.1              |              | Microwave<br>Spectroscopy        | 5 <sub>-1</sub> →6 <sub>-5</sub>  |
| Becker<br>et al. | 1    | 0.744                         | 30.6                                    | 37.6 |                                 |      | 6.9                  | ~7.1              |              |                                  |   |
| Townes<br>et al. | 21   | 0.744                         | 28.2                                    | 37.6 |                                 |      |                      |                   |              |                                  |   |

TABLE II: Comparison with Results Obtained by Other Investigators

Collision Broadening Coefficients are for Full Width at Half Maximum Height  
and Converted to MHz/Torr.

for  $\text{H}_2\text{O}-\text{H}_2\text{O}$  collisions. As it can be seen from eq. (1), by increasing the temperature the linewidth decreases.

A striking discrepancy is, however, observed (Blum et al. [7] and Eng et al [18]) for the lines of highest J which are much narrower than the lower limit which was imposed on the calculated value by choosing a minimum collision diameter equal to the kinetic theory diameter. If Anderson's theory is modified by eliminating the distance of closest approach as pointed out by McClatchey [22] (that is, setting the kinetic theory collision diameter equal to zero) the calculated full width of  $15_{0,15} \rightarrow 16_{1,16}$  is lowered from 1980 MHz to 590 MHz, slightly above the observed value 450 MHz. However, the theoretical justification for this procedure is in question.

Patel [19,13] has measured the full width of two infrared  $\text{H}_2\text{O}$  absorption lines; his result for  $1885.25 \text{ cm}^{-1}$  line is in reasonable agreement with the theoretical predictions. However, a discrepancy for the  $1889.58 \text{ cm}^{-1}$  line exists. We have measured the air broadening coefficient of the same line to be  $6.92 \frac{\text{MHz}}{\text{Torr}}$ .

The results obtained by conventional spectroscopy are in reasonable agreement with the theoretical calculations. Izatt et al. [2] and Ben-Aryeh [3] have obtained results at temperatures higher than room temperature. The resolution obtained in various regions is between  $0.1$  and  $0.2 \text{ cm}^{-1}$ . The ratio of self-broadening coefficient to air or  $\text{N}_2$ -broadening coefficient can be found from Table II and it can be compared with the re-



sult obtained by Burch et al. [17]. Benedict and Kaplan [5] give a value of 5.49 for intensity weighted value of this ratio.

The microwave measurements are in good agreement with the predicted values. In fact, Benedict and Kaplan obtain the value for  $N_2$  quadrupole moment by forcing a fit to the  $5_{-1} \rightarrow 6_{-5}$  microwave line.

The results obtained in this thesis research indicate that the measured linewidths and strengths of the water vapor absorption lines are in good agreement with predicted values. However, the details of the absorption on the wings of the absorption lines are still in question. Measurements by Long et al. [11] have indicated that the CO laser absorption by water vapor is larger than the predicted values, mainly owing to the fact that the wings of the water vapor absorption line do not follow a Lorentzian behavior [23]. In spite of the fact that modified Lorentzian lineshapes have been used to fit the experimental data [24] more experimental results are needed to clarify the absorption in wings.

Appendix III

COLLISION-INDUCED ABSORPTION IN HE-NE MIXTURE

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Since the initial measurement<sup>25</sup> of infrared absorption (between about 350 and 700 cm<sup>-1</sup>) induced during collision of two dissimilar inert gas atoms, there have been several theoretical studies<sup>26,27,28</sup> which calculate these absorption coefficients quantitatively. Although these studies are in excellent agreement with the experimental results, they contain adjustable parameters<sup>26</sup> and simplify the dynamics of the problem with a number of assumptions.<sup>27,28</sup> Further, (1) the errors introduced by these assumptions are not assessed, and (2) in spite of the prediction by both calculations<sup>27,28</sup> that the He-Ne absorption coefficient at 200 cm<sup>-1</sup> equals or exceeds its value in the 350-700 cm<sup>-1</sup> range, Bosomworth and Gush,<sup>29</sup> in a setup similar to that of Ref. 1, were not able to detect any absorption in the 200 cm<sup>-1</sup> range.

In this letter we present a calculation of the He-Ne absorption coefficient which uses no adjustable parameters and treats the dynamics without any approximation, and yields a value which is two orders of magnitude smaller than the experimental value of Ref. 25 and the two calculations<sup>27,28</sup> which compute the He-Ne absorption coefficient. Our calculation inputs the He-Ne interatomic potential, and the induced dipole moment as a function of He-Ne internuclear separation. The He-Ne potential used was a Lennard-Jones (6-12) potential<sup>30</sup> with well depth of  $2.32 \times 10^{-15}$  ergs and a minimum at 3.05 Å. These parameters for the L-J 6-12 potential, obtained from atomic beam experiments, are in good agreement with values derived from transport properties.<sup>31</sup> The dipole moment function  $\mu(r)$  was<sup>32</sup>

$$\mu(r) = Ae^{-\alpha r} + \frac{B}{r^7} \quad (1)$$

where A and  $\alpha$  were taken from Matcha and Nesbet's<sup>33</sup> molecular Hartree-Fock calculation, and B was taken from the long-range dispersion calculation of Whisnant and Byers Brown.<sup>34</sup> The two terms in Eq. (1) take into account



the induced dipole moment due to overlap of charges, and due to dispersion forces between nonoverlapping charges. Although it is not clear that the two contributions simply add, this usual practice yields the best purely theoretical (i.e., without adjustable parameters) dipole moment function currently available, and thus its consequences would seem of interest.

Lacey and Byers Brown have recently advanced toward a better theoretical dipole moment function, in their computation<sup>35</sup> of the overlap contribution at intermediate distances ( $>4a_0$ ), by approximating it by electron exchange between two undistorted Hartree-Fock atoms. This calculation has some features which differ from the Matcha-Nesbet calculation, among them its inclusion of electron correlation effects, and it would have been of interest to see how these features alter the present results. We were not able to do this, however, because the dipole moment function of Ref. 11 is not calculated for small enough values of internuclear distance. In several instances the dominant contribution to the absorption coefficient comes from collisions for which the classical turning point is less than the minimum (4 a.u.) interatomic distance for which the Lacey and Byers Brown dipole moment is available; nor is it apparent how to connect these results to the rather different shorter-distance results of Matcha and Nesbet. The important point is that both the interatomic potential and the dipole moment function used in this calculation are the results of careful and extensive studies.

The absorption coefficient  $\alpha(\omega)$   $\text{cm}^{-1} \text{ amagat}^{-2}$  at frequency  $\omega$  at temperature  $T = (k_B \beta)^{-1}$  where  $k_B$  is the Boltzmann constant can be written as<sup>36</sup>

$$\alpha(\omega) = n^2 \frac{16\pi^2\omega}{3c} \beta^2 \hbar(2M)^{-1/2} \int_0^\infty dE (E + \hbar\omega)^{-1/2} e^{-\beta E} \left[ 1 - \left(1 + \frac{\hbar\omega}{E}\right)^{1/2} e^{-\beta \hbar\omega} \right] \times I(k_i, k_f) \quad (2)$$

where  $n$  is the number of atoms at 1 amagat density ( $2.678 \times 10^{19}$ ),  $M$  is the reduced mass,  $k_i = (2ME)^{1/2}/\hbar$  is the initial relative wave vector,  $k_f = (k_i^2 + \frac{2M}{\hbar^2}\omega)^{1/2}$  is the final relative wave vector determined by energy conservation,

$$I(k_i, k_f) = \sum_{\ell} \left[ \ell I_{\ell, \ell-1} + (\ell+1) I_{\ell, \ell+1} \right] \quad (3)$$

is the sum over the partial waves of the integrals

$$I_{\ell, \ell+1} = \left( \int_0^{\infty} R_{\ell}(k_f) R_{\ell+1}(k_i r) \mu(r) dr \right)^2 \quad (4)$$

where  $\mu(r)$  is the dipole moment function and  $R_{\ell}(kr)$  are the solution of the differential equation.

$$\frac{d^2}{dr^2} R_{\ell}(kr) + \left[ k^2 - \frac{\ell(\ell+1)}{r^2} - \frac{2M}{\hbar^2} V(r) \right] R_{\ell}(kr) = 0 \quad (5)$$

with boundary conditions

$$\lim_{r \rightarrow 0} R_{\ell}(kr) = 0 \quad (5a)$$

$$\lim_{r \rightarrow \infty} R_{\ell}(kr) = \sin(kr - \frac{\ell\pi}{2} + \gamma_{\ell}) \quad (5b)$$

$\gamma_{\ell}(k)$  being the phase shift of  $\ell$ th partial wave with energy  $\hbar^2 k^2 / 2M$  in potential  $V(r)$ . In equation (2), we take the probability that two atoms collide with relative momentum  $k$  as proportional to  $k f(k) dk$ , where  $f(k)$  is the distribution function. In previous literature this probability was taken proportional to  $f(k) dk$ . This accounts for somewhat different factors in the expression for the absorption coefficient than commonly encountered. The overall uncertainty in the value of  $\alpha(\omega)$  due to the various

steps in the computation appears to be less than 10%.

Table 1 compares the result of our calculation with the measurements of Kiss and Welsh<sup>25</sup> as well as other calculations. There is a disparity of about two orders of magnitude between the present calculation and earlier work. Of our two inputs, the interatomic potential is probably more reliable. As pointed out earlier, the parameters for this quantity obtained from atomic beam work and from measurement of transport properties are in good agreement. In addition, limited calculations using the Matcha-Nesbet exponential repulsive potential<sup>33</sup> in place of the L-J 6-12 potential, gave us essentially the same results.

Our second input, the dipole moment function of Eq. (1), is pieced together from two calculations. The part involving the charge overlap, i.e., the Matcha-Nesbet part, has also been calculated by Lacey and Byers Brown,<sup>35</sup> with results (where the interatomic distances of the two calculations overlap), of opposite sign and about double the magnitude; the difference presumably due to the inclusion of electron correlation. A rough calculation indicates that a doubled and sign-reversed overlap contribution throughout would about double our calculated results, and thus not resolve the two orders of magnitude discrepancy. For such a resolution, there would appear two possibilities: (1) Electron correlations increase by about an order of magnitude the Matcha-Nesbet overlap results at short distances. (2) The failure of Bosomworth and Gush to detect any absorption around  $200\text{ cm}^{-1}$  suggests that earlier experiments may involve errors. On this view, the large discrepancy between previous calculations<sup>27,28</sup> and the present one would be accounted for by their adjustable parameters. Tanimoto,<sup>28</sup> for example, determined the factor corresponding to A in Eq. (1) by demanding that his calculations agree with the experiment of Kiss and Welsh at  $400\text{ cm}^{-1}$ . Two



parameters in Ref.27 were determined by requiring the experiment and theory to agree at  $500\text{ cm}^{-1}$  and  $575\text{ cm}^{-1}$ . We remark that if the first explanation obtains, it would be of interest for the salient and knotty field of electronic correlation in molecules: collision-induced absorption in He-Ne would depend principally on such correlations, and thus provide a sensitive testing-ground for theories of correlation. Indeed, the temperature dependence of the absorption coefficient would rather directly probe the distance dependence of the correlations. Table II gives the calculated temperature dependence of the absorption coefficient in the 250-400 °K range.

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TABLE I

Value of the collision-induced absorption coefficient ( $\text{cm}^{-1} \text{ amagat}^{-2}$ ) for He-Ne mixture at room temperature.

| Transition Frequency ( $\text{cm}^{-1}$ ) | Present Calc.        | Kiss and Welsh (Ref. 1) | Levine-Birnbaum* and Levine (Ref. 3) | Tanimoto (Ref. 4)    |
|---|----------------------|-------------------------|--------------------------------------|----------------------|
| 200                                       | $4.0 \times 10^{-9}$ | ---                     | $2.0 \times 10^{-7}$                 | $7.8 \times 10^{-7}$ |
| 400                                       | $4.1 \times 10^{-9}$ | $2.6 \times 10^{-7}$    | $1.7 \times 10^{-7}$                 | $2.6 \times 10^{-7}$ |
| 600                                       | $2.3 \times 10^{-9}$ | $0.7 \times 10^{-7}$    | $0.8 \times 10^{-7}$                 | ---                  |

\* Levine-Birnbaum and Levine results differ about by 10%. We give the average above.

TABLE II

Value of the collision-induced absorption coefficient ( $\text{cm}^{-1} \text{ amagat}^{-2}$ ) for He-Ne mixture as function of temperature.

| Temperature<br>°K | Transition Frequency |                      |                      |
|-------------------|----------------------|----------------------|----------------------|
|                   | 200 $\text{cm}^{-1}$ | 400 $\text{cm}^{-1}$ | 600 $\text{cm}^{-1}$ |
| 250               | $3.8 \times 10^{-9}$ | $3.3 \times 10^{-9}$ | $1.7 \times 10^{-9}$ |
| 298               | $4.0 \times 10^{-9}$ | $4.1 \times 10^{-9}$ | $2.3 \times 10^{-9}$ |
| 350               | $4.3 \times 10^{-9}$ | $4.8 \times 10^{-9}$ | $3.0 \times 10^{-9}$ |
| 400               | $4.4 \times 10^{-9}$ | $5.5 \times 10^{-9}$ | $4.5 \times 10^{-9}$ |



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